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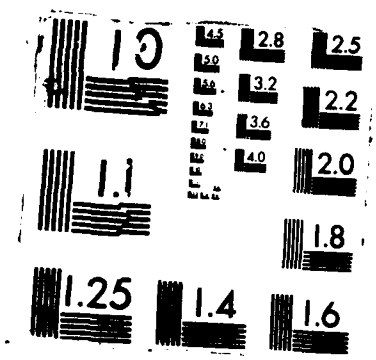

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Technical Report No. 9

Reactor Experiments at the University of Minnesota

by

Edward A. Fletcher

Prepared for Presentation

at

Third Meeting of the International Energy Association
on Solar Fuels, Chemicals, and Energy Transport

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18. SUPPLEMENTARY NOTES

Extended abstract of invited lecture to Third Meeting of the International Energy Association at Sandia National Laboratory, Albuquerque, NM, March 5, 1987.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Solar, electrolysis, metallurgy, zinc, zinc oxide, solar thermal, solar thermoelectrochemical, water splitting, separation devices, reactors

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Reactors are described and operating experience achieved with them in a 4.2 m solar furnace are reported. Water splitting, recovery of hydrogen and sulfur from hydrogen sulfide, electrolysis of zinc oxide in vapor and liquid phases, oil recovery from shale, and fixing atmospheric nitrogen, are discussed.

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Extended Abstract (without photographs) of invited talk delivered at Sandia National Laboratory to Third Meeting of the International Energy Association on Solar Fuels, Chemicals and Energy Transport.

I. Everyone here already knows this, but just for the record:

Solar thermal can be valuable in industrial processes where a large fraction of the value added is the cost of the energy. It is silly to talk about using solar for exotic processes in which a dimes worth of electrical energy is used to produce $10 worth of product. Even if you reduce the energy cost to zero, you haven't improved the process.

Solar thermal should be considered in industrial processes whose energy costs are high. For example:

1. The Sandia-Weizmann CH_4-CO_2 reforming process.

2. Hydrogen production from water and the production of hydrogen and sulfur (or ammonia and sulfuric acid) from H_2S.

3. Electrolytic processes akin to the Hall process for producing metals from their ores. In these processes, concentrated sunlight can approach its real thermodynamic potential in replacing electric power.

4. Direct smelting and reduction of ores.

5. Other industrial processes which traditionally use large electric furnaces, the production of phosphorus, carbides, and nitrides, for example.

6. High temperature processes where cleanliness is important and electric furnaces and plasma generators are dirty, such as in sintering and processing refractory materials.

II. We already know that a great many things can and have been done with solar. In our lab we have used a solar furnace to:

1. Split Water.

2. Produce hydrogen and sulfur from H_2S.

3. Electrolyse ZnO both in liquid solutions and in the gas phase, as well as reduce it directly with carbon.

4. Recover oil from shale.

5. Fix atmospheric nitrogen as NO.

Why isn't industry beating a path to our doorstep? We haven't yet developed even a set of good guidelines for building reactors for solar processes and linking them to the collectors.

III. Conventional chemical engineering has had 100 years in which to develope efficient processes. But, because of the cheapness of energy, it hasn't done nearly as good a job as it should have. Nevertheless, it's come a long way since French and German engineers, who didn't understand the thermodynamics of the process, kept building bigger and bigger blast furnaces in a fruitless effort to improve their yields.

Solar hasn't had time to develope even "energy-inefficient" processing systems, and not much effort has even gone into it so far, but it is essential that we do learn how to build and operate systems which can take advantage of inherent superiority of sunlight as a source of high-temperature process heat if we hope to make ourselves attractive to industry.

IV. At Minnesota, we have been trying to get things started and stir up interest. We (mainly Rich Diver and a group of students who have followed him) built a research furnace (SLIDE 1), and an inexpensive calorimeter with which we measured its performance, (SLIDE 2).

That, incidently, has been the extent of our interest in the performance of solar furnaces, per se, although we have learned that you can sometimes make a good thing too good (SLIDE 3). These are "bad" mirrors and these are "good" mirrors 2.5 hours after sunrise on a frosty morning.

We have been concerned mostly with finding useful things to do with it and learning what problems were going to crop up.

1. We've split water, SLIDE 4, SLIDE 5, and the next slide shows a serious thermodynamic, not to mention safety, deficiency in this simple process (SLIDE 6). A fix to both deficiencies is suggested in the next slide (SLIDE 7). I'll have more to say about zirconia membranes later.

2. Using some of the lore we acquired in our attempts to split water we built a more sophisticated reactor for splitting hydrogen sulfide. It incorporated a heat exchanger. (SLIDE 8 SHOW HOW IT WORKS)

We had great success with this one and a simpler previous model until we had to shut it down suddenly because of an exhaust scrubber failure. Even so, we got yields that were sometimes 70% of the theoretical maximum, and very high conversions, and for this process we can make cautious predictions that if it were starting out in a fresh race with current technology for dealing with hydrogen sulfide, it would be competitive.

SLIDE 9, 10, 11, 12.

Rich Diver designed a next-generation "windowless" reactor, SLIDE 13, and Todd Kappauf is now doing some basic studies on conversion in an ultra-simple laboratory prototype of this design.

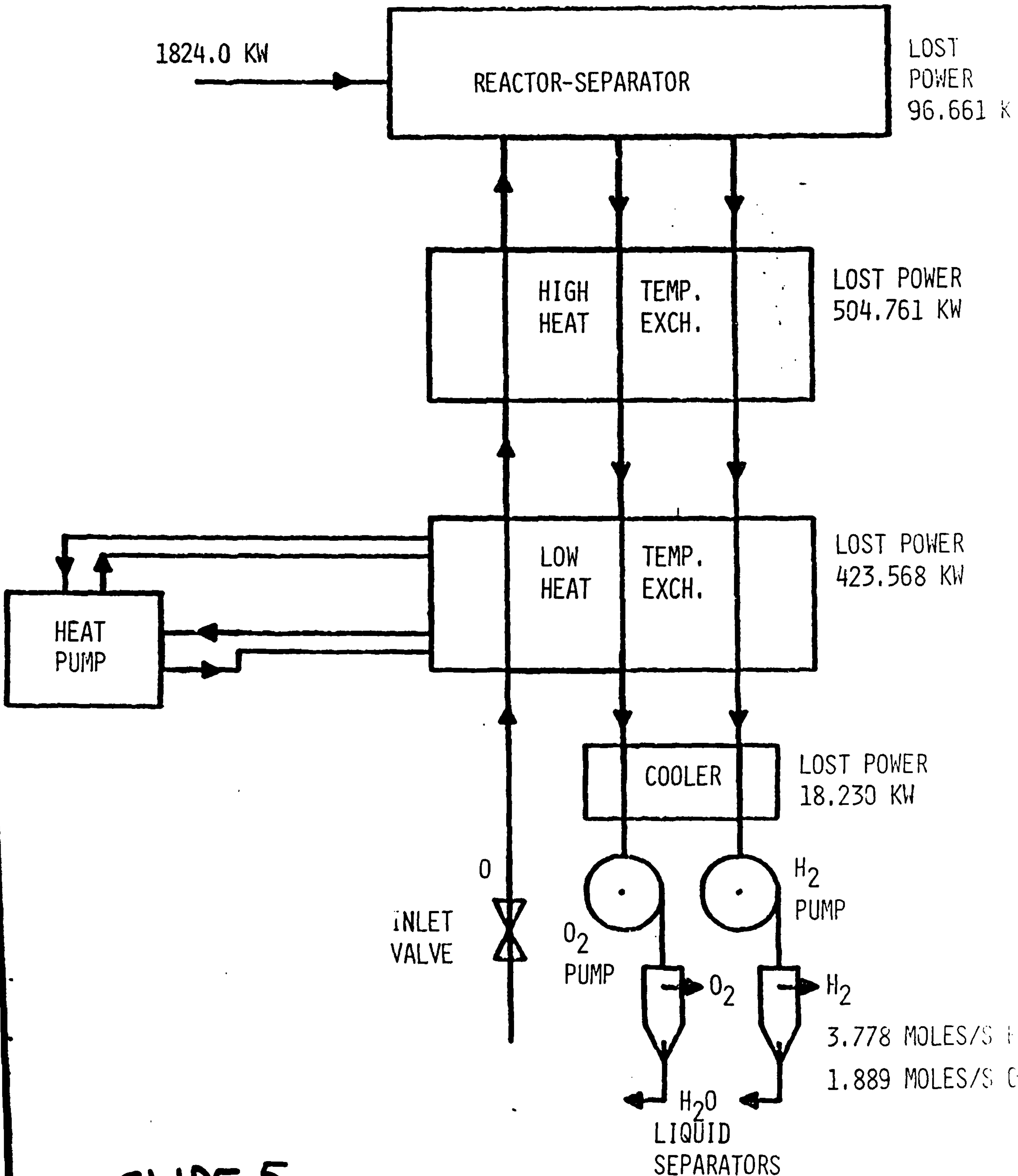
3. Ridvan Berber has used the furnace for retorting shale in both fixed and fluidized beds, with good oil yields (SLIDE 14) as well as ot observe that he can drive off carbon dioxide from the substrate, and Jean Murray is now getting ready to study the behavior of biomass in a bed fluidized with steam (SLIDE 15). We still have a lot to learn about how one should mate a fluidized bed with a solar furnace.

4. Some of our most difficult work has been aimed at the smelting and electrosmelting of metallic oxides. Frank Macdonald started that and it's now being carried on by Bob Palumbo, Kent Scholl, and Aldo Steinfeld. Matching up different kinds of electrolysis processes with solar furnaces presents us with many interesting problems. The next five slides show some of the things that we have been doing. (SLIDES 16, 17, 18, 19, 20). During the course of these experiments we've done a lot of work with graphite, and we've also learned that if you make the temperature high enough, with graphite you can make carbides, just as you can in an industrial electric furnace, or reduce the oxides to the metals. We still have a very long way to go in mating processes like these to solar furnaces, however.

5. One of our most exciting projects is one in which we've been doing exploratory experiments on both the ionic and the electronic semipermeability of zirconia membranes to oxygen. The next slide (SLIDE 21) shows a ring of zinc which Don Parks produced in a small laboratory furnace by electrically pumping the oxygen from zinc oxide vapor at 1650K, where the vapor pressure of ZnO is about 10^{-3} atm.

This has very exciting implications for the development of ROC and electricROC type reactors for water splitting as well as for the reduction of minerals.

6. Finally, (SLIDE 22) people are always asking me why I am doing solar energy research at the University of Minnesota. I certainly envy you all your sunshine. Maybe it's just because the skiing is so good.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COOLER
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18.230 KW
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INLET
VALVE
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PUMP
H_2
PUMP
O_2
H_2
3.778 MOLES/S
1.889 MOLES/S
H_2O
LIQUID
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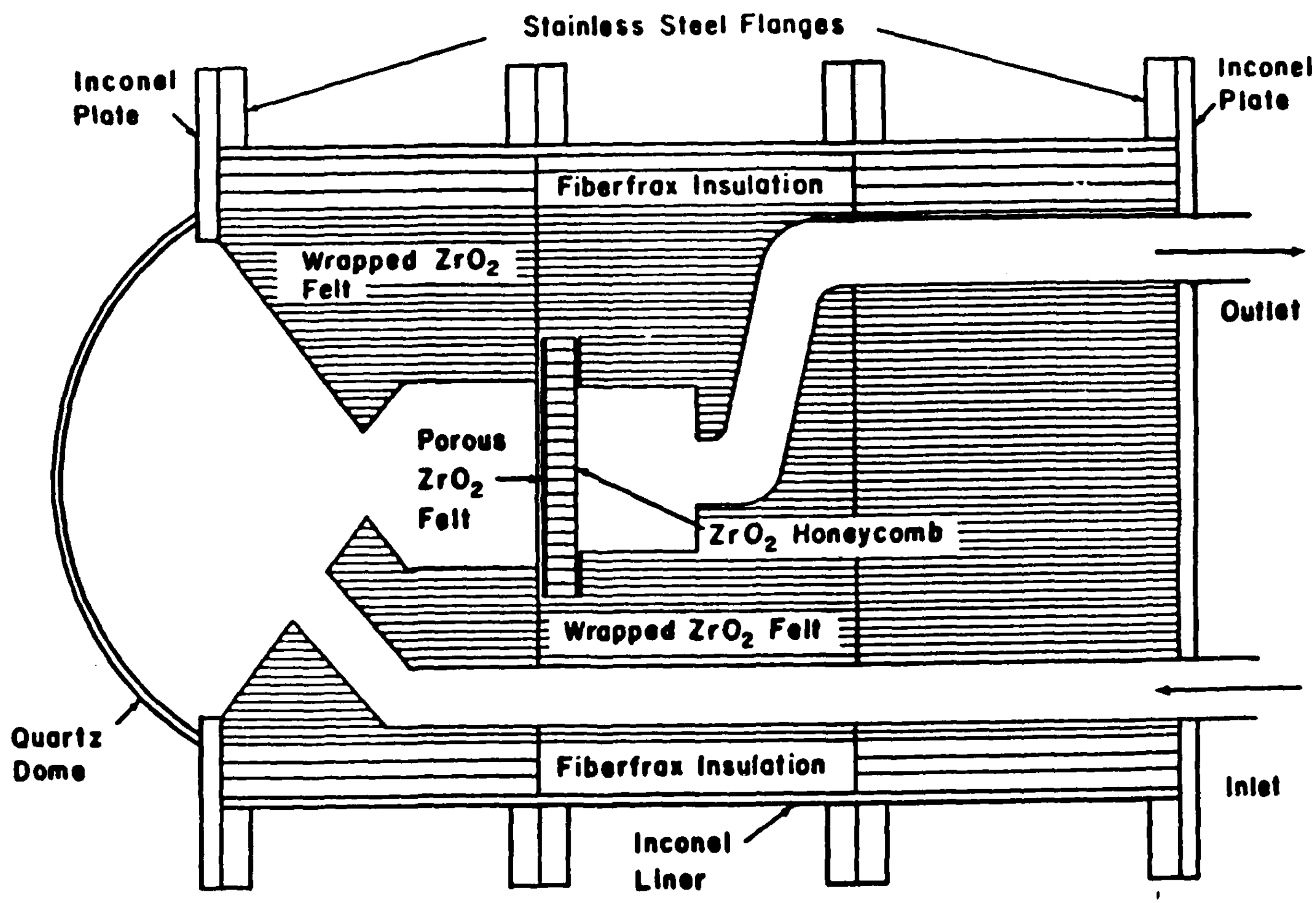
SLIDE 5



Fletcher, Figure 2

SLIDE 6

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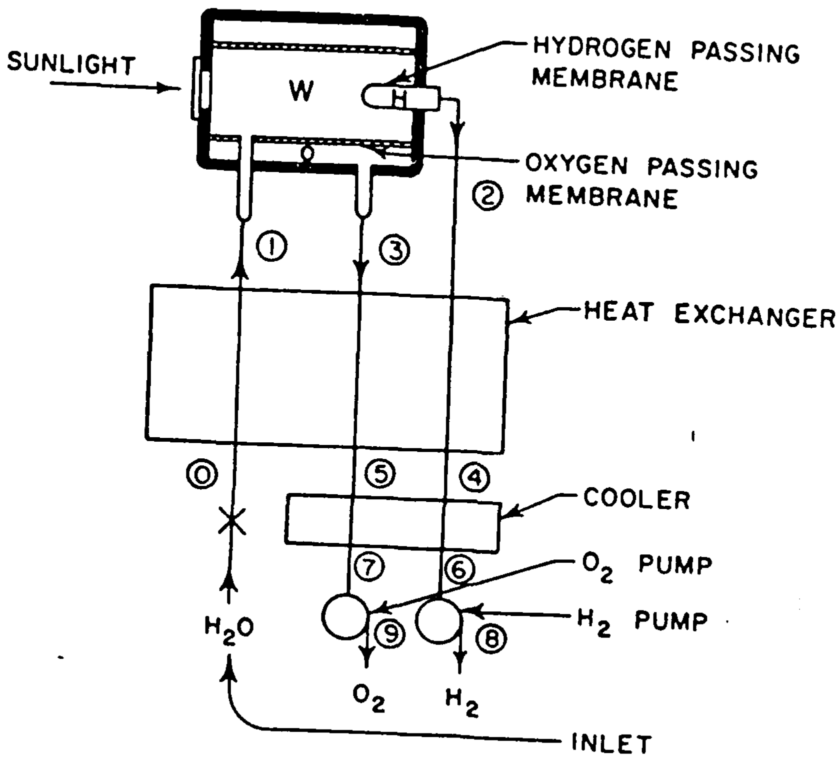

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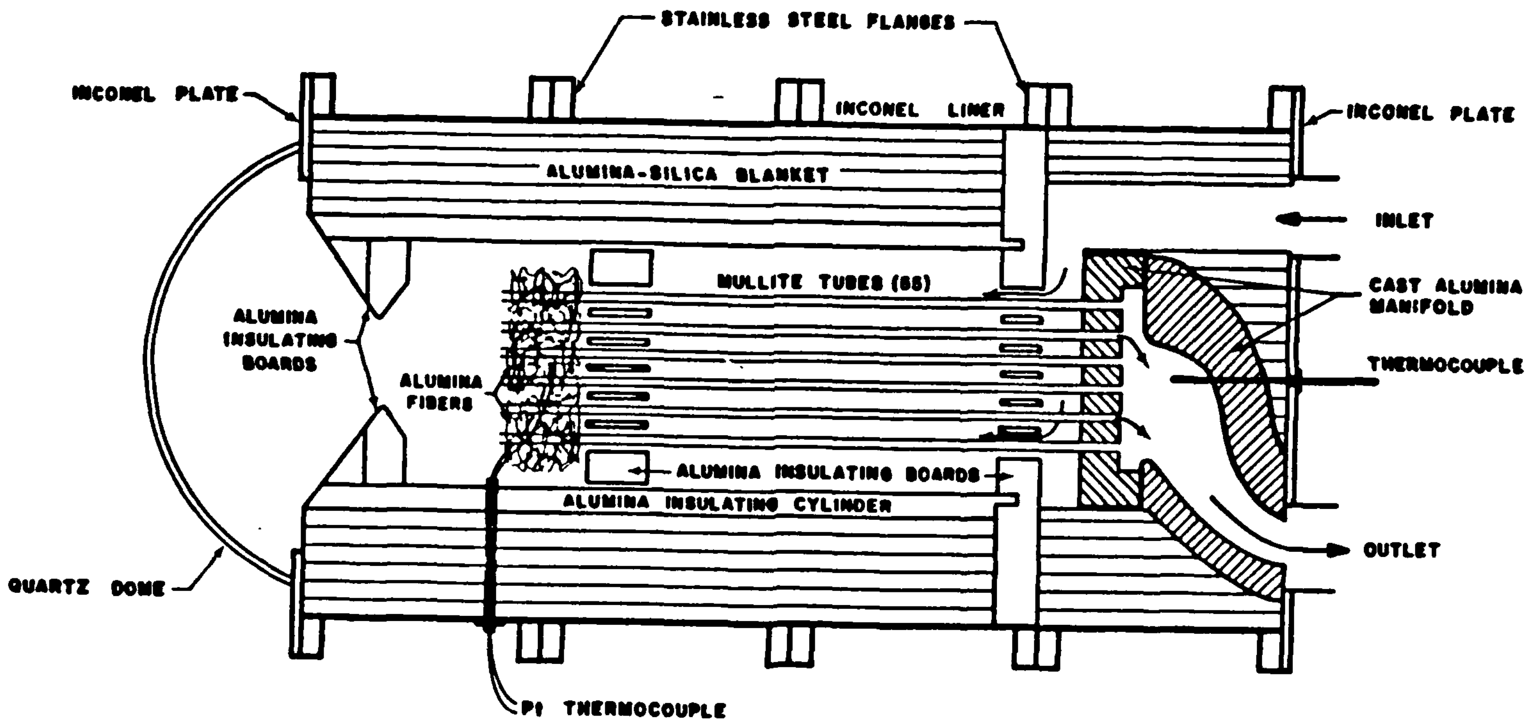
SLIDE 7



Fletcher, Figure 3

SLIDE 8

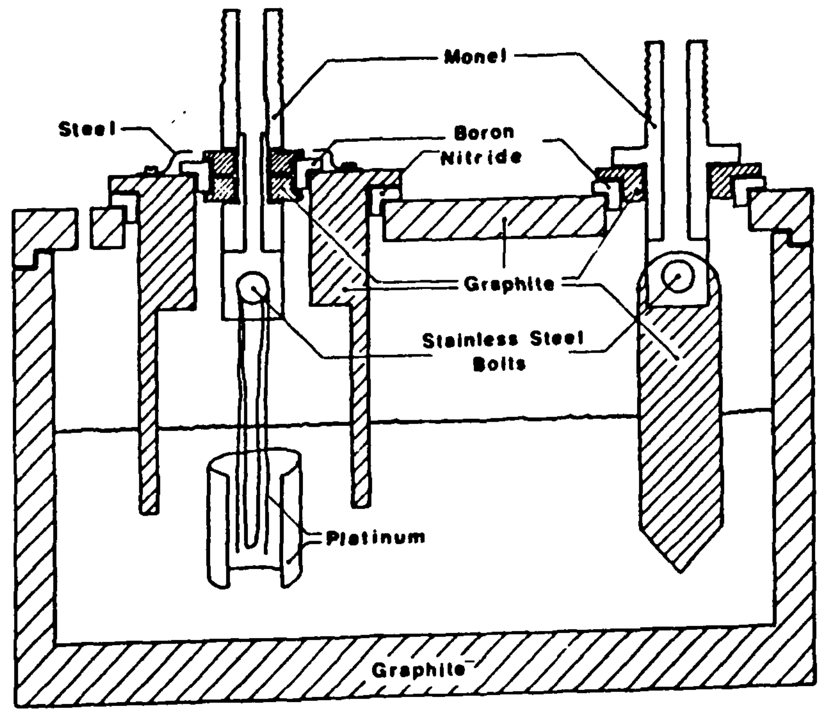


Figure 9 - Detail of the electrochemical cell.

SLIDE 19

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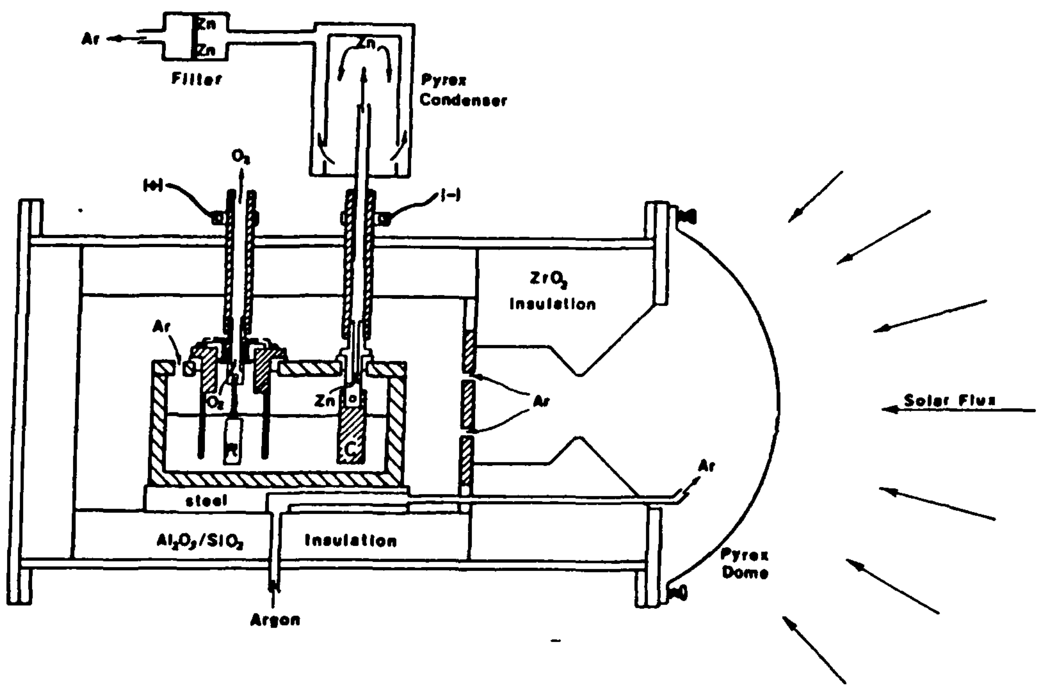

Figure 8 - Schematic of the solar-electrochemical reactor.

SLIDE 20

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